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CATHODIC REDUCTION OF PASSIVE FILMS ON IRON IN BORATE AND PHOSPHATE BUFFER pH 8.4: DIFFERENT MECHANISMS REVEALED BY *IN SITU* TECHNIQUES

P. Schmuki[1], S. Virtanen[2], and H.S. Isaacs[3]

[1] Chair for Surface Science and Corrosion (LKO), Department for Material Science Friedrich-Alexander University Erlangen-Nuremberg, D-91058 Erlangen, Germany

[2] Institute for Materials Chemistry and Corrosion, Swiss Federal Institute of Technology, ETH-Hönggerberg, CH-8093 Zürich, Switzerland

[3] Materials Science Division, Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973, USA

ABSTRACT

The electrochemical behavior of passive Fe and thin, sputter-deposited films of Fe_2O_3 was studied in borate and phosphate buffer pH 8.4 solutions. Cyclic voltammograms and in situ light absorption measurements - which enable the monitoring of the oxide film thickness - indicate a similar behavior of the Fe electrode in both pH 8.4 solution, especially a presence of a oxide-free surface at low cathodic potentials. However, X-ray absorption near edge structure (XANES) studies - which allow a simultaneous monitoring of changes in the samples' average valency and thickness - reveal that the reactions taking place during reduction of the passive film on iron are completely different for the two electrolytes. In borate buffer (pH 8.4), reduction leads to a complete dissolution of the passive film and the end product of reduction is soluble Fe(2+). In phosphate buffer (pH 8.4), there is no dissolution in a direct step to low cathodic potentials, but the resulting reduction product is metallic iron. Hence, the formation of the bare oxide-free metal surface at cathodic potentials takes place by different mechanisms in the two pH 8.4 solutions, depending on the type of anion present in the solution.

INTRODUCTION

The passivity of iron has been studied by many authors using different electrochemical, *ex situ* and *in situ* analytical techniques [for a recent review see Ref. (1)]. One method to monitor changes in the oxide film thickness *in situ*, is light absorption measurement by a differential reflectance technique, as shown by Büchler et al. (2). Another interesting method to study solid/liquid-interfaces, is the *in situ* X-ray absorption near edge structure (XANES), which has been employed to study the electrochemical behavior of thin film iron electrodes (3-6) as well as stability and dissolution of thin film oxide samples used as models for passive films (7-

10). As these studies showed, *in situ* XANES has great potential to elucidate mechanisms of electrochemical reactions in a detailed way, since changes in the average oxidation state as well as dissolution can be monitored simultaneously.

The most widely studied passive Fe/electrolyte systems are Fe in borate buffer (pH 8.4) and 0.1 M NaOH. To further investigate the influence of solution chemistry, Oblonsky et al. carried out XANES experiments on the electrochemical behavior of Fe in different buffer solutions, including acetate and succinate (11).

In the present work, we compare the electrochemical behavior of Fe in borate and phosphate buffer solutions, both at pH 8.4 using the *in situ* light absorption and XANES techniques. Apart from the basic question if the anion type influences the reaction mechanisms, it is also of interest to compare the different experimental methods and their advantages/disadvantages for the study of electrode/electrolyte-interfaces.

The system Fe/phosphate has generally been of a considerable interest, since phosphates are commonly used as corrosion inhibitors for iron. Earlier studies of the system Fe/phosphate have mainly been concerned on the nature of the corrosion films formed on Fe in phosphate-containing solutions. The methods employed include electron diffraction (12), surface analysis (Auger electron spectroscopy) (13), ellipsometry (13, 13), LASER Raman spectroscopy (15), and Mott-Schottky analysis (16). The results of all these studies are in good agreement in showing that the films formed in phosphate-containing solutions on Fe contain phosphate-species. The detailed composition of the films, however, depends on the composition of the solution and passivation conditions (e.g. time, potential). The aim of the present study, however, was not *a priori* to study the composition of the corrosion products, but to clarify the influence of the solution chemistry (borate vs. phosphate) on the reduction behavior of the passive film on Fe.

EXPERIMENTAL

Thin iron films (100 Å) were evaporated on Mylar (6 µm), onto which a thin layer of Ti (~ 200 Å) was previously evaporated to establish a back contact to the samples. The base pressure in the chamber before evaporation was $<10^{-8}$ Torr, achieved with a titanium sublimation pump. Thin iron oxide films (20 nm thick) were prepared by r.f. sputter deposition using a Fe_2O_3 target. Similarly, the films were deposited on a Mylar (6 mm) / Ta (~200 Å) structure. The r.f. sputtering system has been described elsewhere (17). Before each deposition, the sputter chamber was evacuated to a pressure of 4 to 7 x 10^{-4} Pa, and deposition was carried out in pure Ar (99.998%). Details of the characterization of the samples are given elsewhere (18).

Cyclic voltammograms were measured in a flow cell described in ref. (2). The differential reflectance technique for the light absorption measurement using a heCd LASE with a wavelength of 325 nm has also been described in ref. (2). The electrochemical cell used for XANES studies has been described earlier (5, 19). XANES measurements were carried out in situ during the electrochemical treatment of the samples. The electrolyte solutions were continuously de-aerated with a stream of Ar bubbles. The potentials were measured and are reported against a saturated mercury-sulfate reference electrode (MSE, ~ +0.4 V (SCE)). A platinum wire was used as a counter electrode. The solutions were prepared from reagent grade chemicals and distilled water.

XANES measurements were carried out at Beamlines X10C and X18B at the National Synchrotron Light Source at Brookhaven National Laboratory. The energy scale was calibrated by taking the peak in the first derivative of the spectrum from an iron foil as the position of the Fe K edge at 7112 eV. *In situ* measurements on the electrochemically controlled samples were made using fluorescence detection set up with a Canberra 13-element solid-state detector. Further details of the geometry are given in reference (5).

RESULTS AND DISCUSSION

Cyclic voltammetry

Figure 1 compares the cyclic voltammograms (scan rate = 10 mV/s) of Fe in borate buffer and phosphate buffer solutions, both at pH 8.4. The current densities in the region of the active/passive-transition are significantly lower in the phosphate solution than in the borate solution. Further, the second oxidation peak is shifted to lower potentials in phosphate solution compared to borate buffer. This second oxidation peak in the borate buffer stems from the oxidation of Fe(II) to Fe(III) (2, 21-23). Nevertheless, the voltammograms in the borate and phosphate buffer are similar in that they show identical current densities in anodic and cathodic sweeps in all cycles. This in contrast to voltammograms of Fe in 0.1 M NaOH, where the current densities in the oxidation and reduction peaks increase steadily with each cycle - this behavior has been discussed in detail in ref. 20.

Light absorption measurements

In Fig. 2 the light absorption data recorded simultaneously with the voltammograms are shown. In both cases, the light absorption data show a similar behavior. In the passive range, a linear dependence between the absorption intensity and potential is observed, indicating film growth. After the inversion of the sweep direction, the absorption remains constant until the region of cathodic reduction of the iron oxide film. Remaining 5 minutes at the cathodic potential, results in the same initial absorption of the surface. In multiple cycles, an identical behavior in all cycles is found not only in the cyclic voltammograms but also in the absorption behavior, indicating that the surface returns to its original state at the low cathodic potential (i.e., in both cases a formation of a bare metal surface takes place at the cathodic potentials). These results hence demonstrate that the non-changing current densities from cycle to cycle in the cyclic voltammograms in borate and phosphate solutions can be ascribed to each cycle starting with bare metal in contact with the solution at the most negative potential.

However, even though this data clearly indicates the absence of a strongly absorbing ferric oxide on the surface at the cathodic potentials, it does not allow to draw any conclusions on the mechanism of the formation of a bare metal surface.

XANES experiments on Fe electrodes

Figures 3 and 4 show the XANES spectra obtained with Fe after a series of potential steps during passivation and reduction in borate buffer (Fig. 3) and phosphate buffer (Fig. 4).

The spectra were measured after 5 min polarization at each potential. For thin film samples, the edge height corresponds to the total amount of iron in the sample. The edge position depends on the oxidation state of the element. Hence, XANES spectra detect both material loss (drop in edge height) and changes in the valency (shift in the edge position).

In borate buffer, during the first potential step to -1.6 V MSE, the air-formed oxide film dissolves, leading to a drop in edge height (Fig. 3). During the formation of the passive film at +200 mV, no material loss is observed, as has also been shown by others (3, 11). This passive film is dissolved by a subsequent step to -1.6 V, as indicated by a drop in edge height. In Fig. 3b) the spectra are normalized after background subtraction to unity edge height, and are shown with an expanded energy scale near to the edge position. It is clear that a potential step to -1.6 V decreases the sample's average valency (negative edge shift), resulting from the removal of the oxide layer, so leaving only the metal in the path of the beam. By polarizing at +200 mV MSE, a new passive film is formed, which increases the average valency of the Fe in the sample (positive edge shift). The changes in the edge position are not very large, because the signal from the underlying metallic iron dominates the spectrum, and the contribution from the thin passive film is relatively small. The peak in the first derivative of the spectrum measured at -1.6 V MSE is 7112.0 eV which is identical to that measured for an Fe foil; hence the sample contains no oxide in the reduced state.

XANES spectra during potential stepping between the passive region (+0.2 V) and the reduction region (-1.6 V) in phosphate buffer, pH 8.4, are shown in Fig. 4. Unlike to the behavior in borate buffer at the same pH, no changes in the edge height - hence, no dissolution - occur during potential stepping. However, the spectra with an expanded energy scale near to the edge region (4b) reveal that in phosphate buffer spectra in the reduced state are identical to the spectrum of metallic iron. The peak in the first derivative of the spectrum measured at -1.6 V MSE in phosphate buffer is 7112.0 eV. Therefore, the passive film on iron has been converted into metallic iron in a solid-state reaction during reduction

These results demonstrate that the formation of a bare metal surface in contact with the solution at the most negative potential takes place by completely different mechanisms in the two solutions: In borate buffer, complete dissolution of the passive film by reduction reveals the bare metal surface. In phosphate buffer, conversion of the passive film into metallic iron results in the same effect, i.e., re-formation of a bare metal surface during reduction (due to oxide conversion, and not to oxide dissolution).

Solution chemistry therefore plays a dominant role in determining which reactions take place during reduction of the passive film on iron, also in the case of identical pH solutions.

XANES experiments on Fe_2O_3 films

The conversion of the passive film on iron into metallic iron during reduction has been discussed previously (24-27). However, other investigations [including our XANES studies (7)] did not show evidence for the formation of metallic iron during reduction of the passive film in borate buffer (28, 29). The specific case of phosphate solutions has scarcely been investigated from this point of view. We earlier gave some possible explanations for the controversial findings and/or interpretations on the reduction mechanism of the passive film (7). Since the question of the reduction products is debatable, we performed additional experiments on thin, sputter-deposited films of Fe_2O_3, to obtain more conclusive data on the reduction behavior of iron

oxide films. Since the samples did not initially contain metallic iron, any presence of metallic iron in the spectra must be ascribed to its formation during the experiment.

Figure 5 shows the behavior of a thin film of Fe_2O_3 during a cathodic potential step in borate buffer. The first spectrum measured at -1.6 V MSE was started immediately after stepping to this potential. (The times indicated in Fig. 5 correspond to the time at the start of the spectrum; the time to acquire the complete spectra was 5 min). After 6 min at -1.6 V MSE, the second spectrum shows that the sample has completely dissolved, with no indication of presence of metallic iron during reduction. Galvanostatic reduction experiments showed that this reductive dissolution proceeds via conversion of the Fe_2O_3 into an oxide film with a valency near to Fe_3O_4 (7).

Figure 6 shows the corresponding experiment in phosphate buffer, at pH 8.4; the edge shift is 5.1 eV between the original Fe_2O_3 film at the open-circuit potential and after reduction. The edge position and the shape of the spectra of the reduced Fe_2O_3 sample are identical with an Fe standard (30), verifying the conversion of the iron oxide film into metallic iron during reduction in phosphate buffer solution.

CONCLUSIONS

- The reduction of Fe_2O_3 and the passive film on iron results in different end products depending on the electrolyte's composition. The following reactions were observed:

1) In borate buffer, pH 8.4, the reaction

$$Fe_2O_3 + 6\ H^+ + 2e^- \text{---> } 2\ Fe^{2+}(aq) + 3\ H_2O$$

takes place with a soluble reduction product. Hence, the passive film is completely removed by reductive dissolution.

2) In phosphate buffer, pH 8.4, the reaction

$$Fe_2O_3 + 6\ H^+ + 6\ e^- \text{---> } 2\ Fe + 3\ H_2O$$

leads to metallic iron forming on the electrode. No dissolution of the Fe electrode takes place by a direct step into the stability region of metallic iron.

- *In situ* light absorption experiments identify the presence/absence of oxide films on the surface. However, the method does not enable to conclude on the reaction mechanisms leading to oxide growth/thinning.

- To identify reactions on electrode surfaces during electrochemical experiments, *in situ* monitoring of dissolution and changes in the valency are essential (e.g., with *in situ* XANES).

- Model systems, such as thin oxide films (artificial passive films), can be very helpful in verifying mechanisms of complex real systems.

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REFERENCES

1 A. Davenport, L.J. Oblonsky, M.P. Ryan, and M. F. Toney: J. Electrochem. Soc. 147, 2162 (2000)
2 M. Büchler, P. Schmuki, and H. Böhni: J. Electrochem. Soc. 144, 2308 (1997)
3 A. J. Davenport, H. S. Isaacs, J. A. Bardwell, B. MacDougall, G. S. Frankel, and A. G. Schrott, Corros. Sci., 35, 19 (1993).
4 A. J. Davenport, J. A. Bardwell, and C. M. Vitus, J. Electrochem. Soc., 142, 721 (1995).
5 A. J. Davenport and M. Sansone, J. Electrochem. Soc., 142, 725 (1995).
6 L. J. Oblonsky, A. J. Davenport, M. P. Ryan, H. S. Isaacs, and R. C. Newman, J. Electrochem. Soc., 144, 2398 (1997).
7 P. Schmuki, S. Virtanen, A. J. Davenport, and C. M. Vitus, J. Electrochem. Soc., 143, 574 (1996).
8 P. Schmuki, S. Virtanen, A. J. Davenport, and C. M. Vitus, J. Electrochem. Soc., 143, 3997 (1996).
9 P. Schmuki, S. Virtanen, H. S. Isaacs, A. J. Davenport, H. Böhni, and T. Stenberg, in Surface Oxide Films, J. A. Bardwell, Editor. Proc.-Vol. 96-18, p. 234, The Electrochemical Society, Pennington, NJ, (1996).
10 S. Virtanen, P. Schmuki, A. J. Davenport, and C. M. Vitus, J. Electrochem. Soc., 144, 198 (1997).
11 L. J. Oblonsky, A. J. Davenport, M. P. Ryan, H. S. Isaacs, and R. C. Newman, in Surface Oxide Films, San Antonio, J. Bardwell, Editor. Proc.-Vol. 96-18, p. 223, The Electrochemical Society, Pennington, NJ, (1996).
12 J. E. O. Mayne and J. W. Menter, J. Chem. Soc., 103 (1954).
13 J. B. Lumsden and Z. Szklarska-Smialowska, Corrosion, 34, 169 (1978).
14 W. Kozlowski and J. Flis, Corros. Sci., 32, 861 (1991).
15 C. A. Melendres, N. Camillone, and T. Tipton, Electrochimica Acta, 34, 281 (1989).
16 K. Azumi, T. Ohtsuka, and N. Sato, J. of the Electrochem. Soc., 134, 1352 (1987).
17 P. Vuoristo, PhD Thesis, Tampere University of Technology, Tampere, Finland, (1991).
18 T. Stenberg, P. Vuoristo, J. Keränen, T. Mäntylä, M. Büchler, S. Virtanen, P. Schmuki, and H. Böhni, Thin Solid Films, 312, 48 (1998).
19 M. Kerkar, J. Robinson, and A. J. Forty, Faraday Discuss. Chem. Soc., 89, 31 (1990).
20 P. Schmuki, M. Büchler, S. Virtanen, H. S. Isaacs, M. P. Ryan, and H. Böhni, J. Electrochem. Soc., 146, 2097 (1999).
21 S. Haupt and H.-H. Strehblow, Corr. Sci., 29, 163 (1989).
22 M. E. Vela, J. R. Vilche, and A. J. Ariva, J. Appl. Electrochem., 16, 490 (1986).
23 M. Büchler, P. Schmuki, H. Böhni, T. Stenberg, and T. Mäntylä, in Surface Oxide Films, San Antonio, J. Bardwell, Editor. Proc.-Vol. 96-18, p. 172, The Electrochemical Society, (1996).
24 M. Cohen, Corrosion, 32, 461 (1976).
25 M. Nagayama and M. Cohen, J. Electrochem. Soc., 109, 781 (1962).

26 K. Ogura and T. Majima, Electrochim. Acta, 23, 785 (1978).
27 K. Ogura and K. Sato, Electrochim. Acta, 25, 1361 (1980).
28 T. Tsuru, E. i. Fujii, and S. Haruyama, Corros. Sci., 31 655 (1990).
29 P. Southworth, A. Hamnett, A. M. Riley, and J. M. Sykes, Corros. Sci., 28 (1988).
30 P. Schmuki, S. Virtanen, H. S. Isaacs, M. P. Ryan, A. J. Davenport, H. Böhni, and T. Stenberg, J. Electrochem. Soc., 145, 791 (1998).

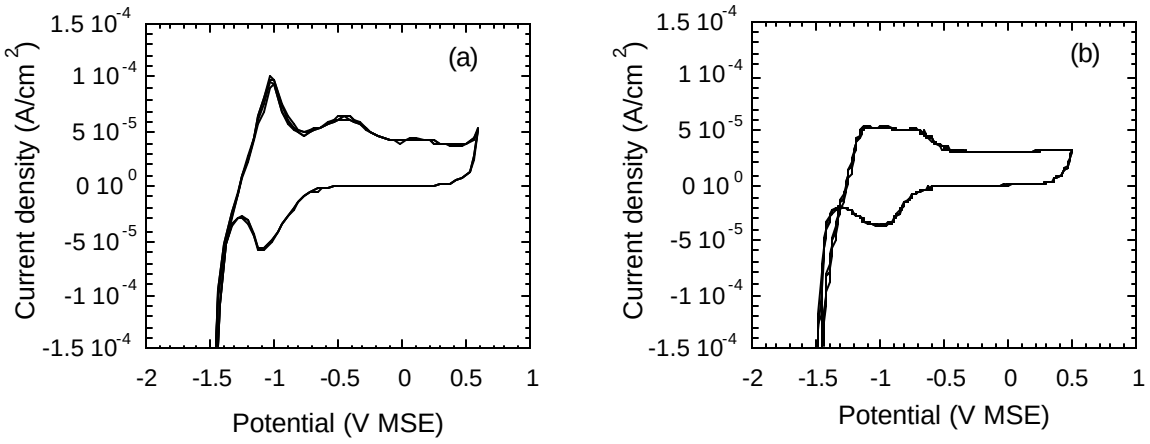

Fig. 1 Cyclic voltammograms (10 cycles, scan rate = 10 mV/s) of Fe in a) borate buffer, pH 8.4, and b) phosphate buffer, pH 8.4

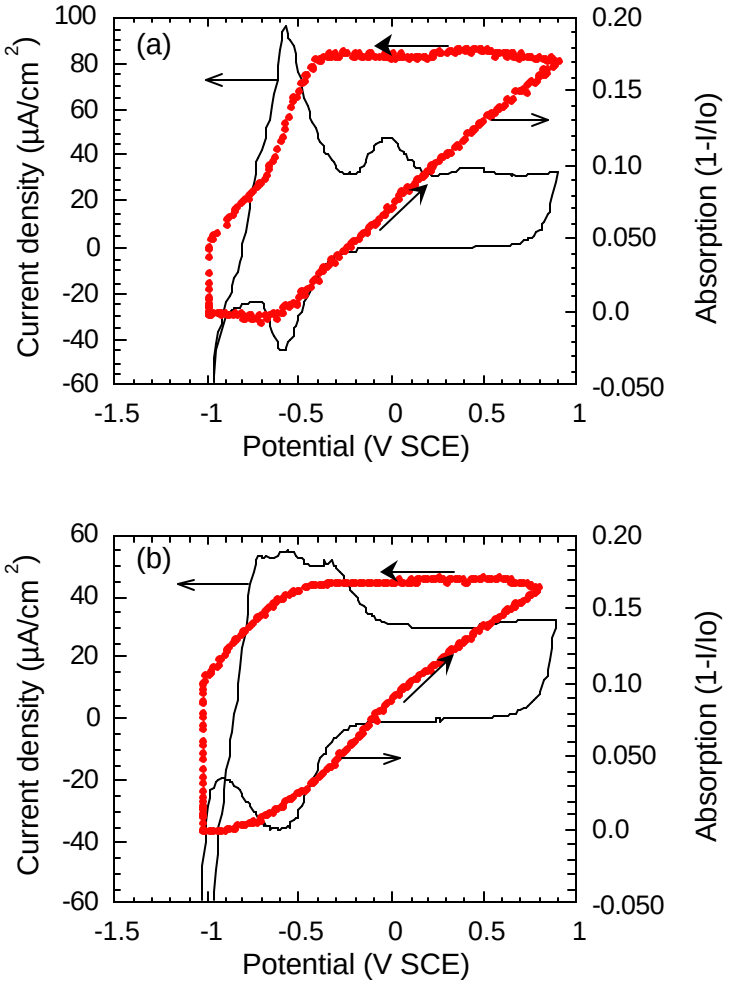

Fig. 2 Cyclic voltammograms (scan rate = 10 mV/s) and simultaneously measured light absorption data of Fe in a) borate buffer, pH 8.4, and b) phosphate buffer, pH 8.4

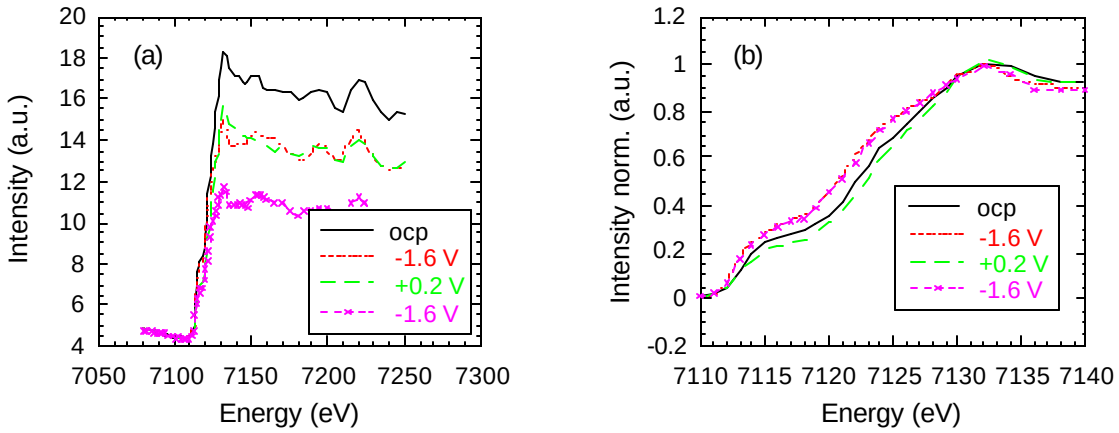

Fig. 3 XANES spectra of an Fe thin film (100Å) during potential steps in borate buffer, pH 8.4. The spectra were acquired after 5 min at each potential.
a) raw data b) normalized data

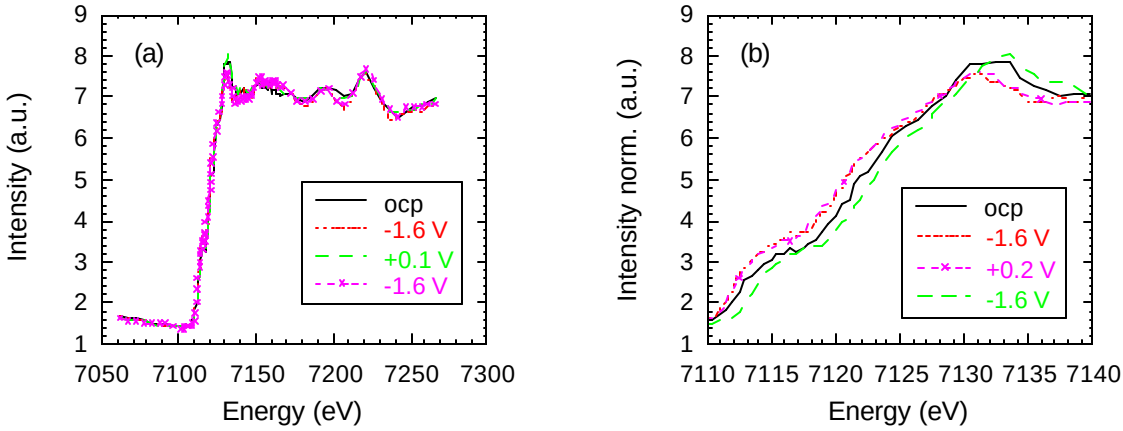

Fig.4 XANES spectra of an Fe thin film (100 Å) during potential steps in phosphate buffer, pH 8.4. The spectra were acquired after 5 min at each potential.
a) whole energy region
b) expanded energy scale near to the absorption edge

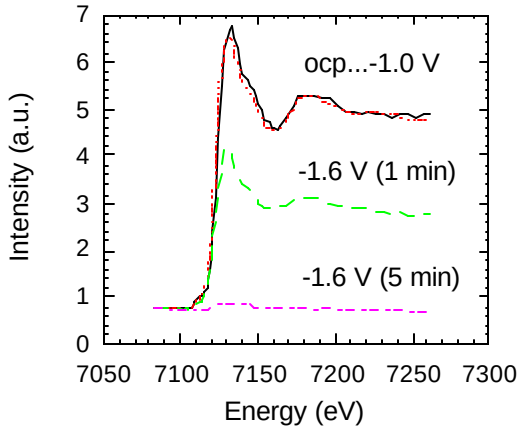

Fig. 5 XANES spectra measured on a thin film (20 nm) Fe_2O_3 sample in borate buffer.

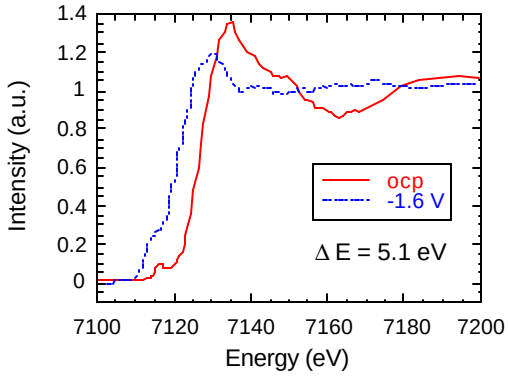

Fig. 7 XANES spectra measured on a thin film (20 nm) Fe_2O_3 sample in phosphate buffer